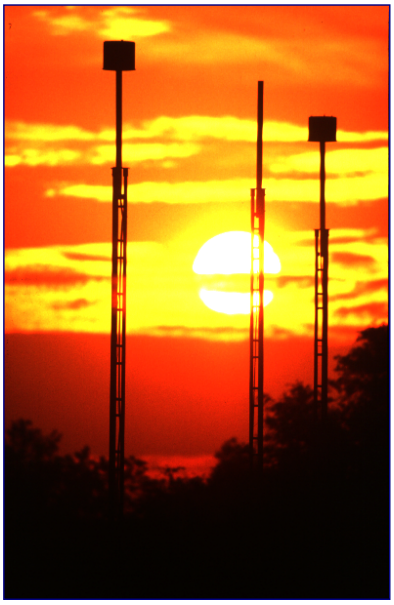
Chapter 2



Concentrations of Sulfur and Nitrogen Species and Cations

CASTNet measurements of sulfur and nitrogen species and cations have been analyzed for the period 1990 through 2000. The measurements show a significant decline in SO_2 and sulfate. Every reference site measured lower concentrations at the end of the 11-year period. The largest decreases were observed in and downwind of the Ohio River Valley. HNO_3, NO_3^-, and total nitrate concentrations show no significant change. NH_4^+ concentrations were slightly lower. Cation concentrations show two general patterns: relatively high Ca^{2+} in the agricultural Midwest and high Na^+ levels in coastal regions.

Air pollutant concentrations measured in 2000 using the CASTNet filter packs include SO_2, SO_4^{2-}, HNO_3, NH_4^+, NO_3^-, total nitrate (HNO_3 plus particulate NO_3^-), and the four cations: Ca^{2+}, K^+, Mg^{2+}, and Na^+. Maps of 2000 annual mean concentrations are presented in this chapter. Maps of quarterly mean concentrations are presented in Appendix B.

Discussion of each of the six primary pollutants includes a map of 2000 annual mean concentrations, a box plot to illustrate the trend in each pollutant over the period 1990 through 2000, and a map of differences in two sets of 3-year average concentrations – 1990 through 1992 versus 1998 through 2000. These two 3-year periods were selected to illustrate air quality before and after the 1995 implementation of the Phase I SO_2 emission reductions. The subsection on cations includes maps of 2000 concentrations.

Sulfur Species

Sulfur Dioxide

Figure 2-1 presents a map of 2000 mean SO_2 concentrations. The highest annual concentrations were observed in and downwind of the Ohio River Valley with six sites showing concentrations above 10.0 μg/m^3. The single highest concentration in the continental United States (19.3 μg/m^3) was observed in eastern Ohio at QAK172. Concentrations measured at CASTNet sites in the western United States were significantly lower than those measured in the East with the exception of the monitor at Hawaii Volcanoes National Park (HVT424), which recorded the highest mean SO_2 concentration (26.3 μg/m^3) of any CASTNet site. See the sidebar following Figure 2-8 for a discussion of SO_2 concentrations at HVT424. The geographic patterns of measured concentrations are similar to the distribution of SO_2 emission sources (Figure 1-4).

The highest annual mean SO_2 concentrations were measured in and downwind of the Ohio River Valley. This region also experienced the largest decline in sulfur dioxide. Measured SO_2 concentrations are related to the geographic distribution of SO_2 emissions.

One of CASTNet's objectives is to monitor trends in air quality and deposition. The trend analyses were prepared using measurements from the 34 eastern reference sites shown in Figure 1-3. Site selection criteria and data interpolation procedures are discussed in Chapter 1. The data from the 34 sites are presented via box plot values for each year for the period 1990 through 2000.

Figure 2-2 presents a box plot illustrating the trend in annual SO_2 concentrations over the 11 years. The intersite variability among the 34 eastern sites is shown graphically by the mean, median, and percentile values of annual concentrations for each year. The box plot shows a sharp reduction in SO_2 concentrations in 1995 and a relatively flat distribution thereafter. This noticeable reduction in ambient SO_2 was produced by a decrease in SO_2 emissions from Phase I electric utilities (see Figure 1-6).

Changes in SO_2 concentrations for the 34 eastern and six western reference sites are presented in Figure 2-3. A site in Ann Arbor, MI (ANA115) was added to the reference site group for the difference maps because of its complete record for the six years that were analyzed. The figure shows concentration differences by comparing two 3-year averages: 1990 through 1992 and 1998 through 2000. The circles in the figure illustrate the changes (in $\mu g/m^3$) from the beginning 3-year period to the ending 3-year period. The legend in the figure provides a scale for gauging the concentration changes. For example, the largest blue circle indicates a reduction of 8.0 $\mu g/m^3$ while the smallest blue circle indicates a reduction of only 0.8 $\mu g/m^3$. In other words, the changes are directly proportional to the size of the circles; the legend provides the scale to gauge the changes (decreases) in the 3-year average concentrations. The map shows that the largest reductions in SO_2 were observed along the Ohio River Valley from southern Illinois to Pennsylvania.

Particulate Sulfate

Annual mean particulate SO_4^{2-} concentrations for 2000 are shown in Figure 2-4. Concentrations above 5.0 $\mu g/m^3$ were observed in a region extending from northern Alabama to southwestern Pennsylvania. The highest concentration (6.8 $\mu g/m^3$) was measured at Sand Mountain, AL (SND152).

Annual mean particulate SO_4^{2-} concentrations for 1991 are shown in Figure 2-5. Comparison of Figure 2-4 with Figure 2-5 illustrates the change in mean atmospheric sulfate concentrations over the past ten years. Over time, the magnitude of the concentrations has decreased and the location of higher concentrations has shifted southward.

The trend in annual SO_4^{2-} concentrations is shown in Figure 2-6. The box plot shows a significant reduction in sulfate over the 11 years.

Figure 2-7 illustrates changes in 3-year average concentrations for the reference sites. The largest circle in the legend signifies a reduction of 2.0 $\mu g/m^3$. The data show consistent decreases in ambient sulfate at all eastern and western sites.

Annual mean SO_4^{2-} concentrations have declined at all 34 eastern reference sites. Maps of sulfate concentrations show the decline in concentration magnitude and also that the region of peak concentrations has shifted from the Ohio River Valley southward. The CASTNet measurements show that sulfate has declined less rapidly than SO_2.

Because the box plots for SO_2 and SO_4^{2-} indicate that sulfate has declined less rapidly than SO_2, an analysis of the relative contribution of sulfate to atmospheric sulfur was performed. Figure 2-8 presents a box plot of the ratio of annual sulfate concentrations (as S) to total sulfur (SO_2 + SO_4^{2-}, as S). The figure shows a slight increase in the mean sulfate fraction over the 11 years.

This figure and the information in Figures 2-2 and 2-6 indicate that the contribution of particulate SO_4^{2-} to total atmospheric sulfur (SO_2 + SO_4^{2-}) has increased slightly. In other words, sulfate concentrations have decreased more slowly than concentrations of SO_2, even though both are produced by SO_2 emissions. Reid *et al.* (2001) discuss a number of possible reasons for this "discrepancy," e.g., different atmospheric

lifetimes of SO_2 and SO_4^{2-}, a change in the oxidizing power of the atmosphere, and a high background concentration of sulfate. These authors also suggest that perhaps there is an incomplete understanding of atmospheric sulfur compounds and the link between SO_2 emissions and aerosol SO_4^{2-}.

Nitrogen Species

Nitric Acid

Figure 2-9 provides a map of annual mean HNO_3 concentrations for 2000. Most of the sites in the eastern United States observed concentrations above 2.0 μg/m^3. The highest concentration (3.7 μg/m^3) was measured in eastern Ohio (QAK172). Concentrations along the Appalachian Mountain chain were variable (from about 1.0 to 3.0 μg/m^3). Joshua Tree National Monument, CA (JOT403) measured the highest concentration (2.7 μg/m^3) in the West.

The box plot shown in Figure 2-10 shows the trend in nitric acid concentrations. The figure shows no significant change over the 11 years.

In 2000, most eastern sites measured HNO_3 concentrations above 2.0 μg/m^3. The highest concentration was observed in eastern Ohio. Data from sites along the Appalachian Mountains show considerable geographic variability – a factor of 3.0 change in concentration levels. These measurements suggest an influence of terrain on concentrations – through exposure, local photochemistry, and V_d. The measurements show no trend in nitric acid, even over the last few years when NO_x emissions have declined.

Changes in 3-year average concentrations over the 11 years are shown in Figure 2-11. Blue circles show reductions and yellow show increases in HNO_3. Decreases were observed in the Northeast from Pennsylvania and Virginia across New England with increases observed at most other reference sites.

Particulate Nitrate

Figure 2-12 depicts 2000 annual mean concentrations of nitrate aerosols. The measured concentrations showed considerable intersite variability among nearby sites. For example, values measured in Pennsylvania varied from 0.5 to 1.8 μg/m^3. The highest concentrations were measured in the agricultural Midwest from Illinois across Indiana, northern Ohio, Michigan, and into Ontario.

The highest nitrate aerosol concentrations were measured in the agricultural states of Illinois, Indiana, and Ohio. All but a few CASTNet sites observed increases in NO_3^-, despite declines in NO_x emissions over the past few years.

Figure 2-13 presents the trend in particulate NO_3^-. The box plot indicates no significant trend.

Figure 2-14 shows changes in 3-year average concentrations over the 11 years. A large majority of CASTNet sites showed increases in particulate nitrate.

Total Nitrate

Annual mean concentrations of total nitrate for 2000 are shown in Figure 2-15. The map shows a region with concentrations above 4.0 μg/m^3 extending across Illinois, Indiana, Ohio, and into northern Kentucky. A mean concentration of 4.1 μg/m^3 was measured at SND152. JOT403 measured a value of 4.0 μg/m^3.

Figure 2-16, which shows the box plot for total nitrate, indicates no trend.

Figure 2-17 shows the changes in three-year average concentrations of total nitrate. The pattern is similar to changes in HNO_3, i.e., decreases in the Northeast from Pennsylvania and Virginia to New England with increases in HNO_3 concentrations at most other reference sites.

Because nitrogen oxide emissions and concentrations of nitrogen species have not changed significantly over the past 11 years, an analysis of the relative contribution of nitrogen and sulfur to atmospheric pollution was performed. A box plot of

the ratio of nitrogen to sulfur (in molar units) from the database for the 34 eastern reference sites is presented in Figure 2-18. The plot shows an increase in the nitrogen fraction. The annual nitrogen-sulfur ratios follow the changes in SO_2 and NO_x emissions discussed in Chapter 1. This information suggests a change in the contribution of sulfur and nitrogen pollutants to atmospheric chemistry and their resulting impact on acid deposition, fine particles, and regional haze.

Particulate Ammonium

Figure 2-19 presents 2000 annual mean concentrations of NH_4^+. Most of the eastern sites observed concentrations above 1.0 μg/m^3. Peak values were observed in the Midwest, Pennsylvania, and in northern Alabama. The data show downward gradients from Pennsylvania across New England, from northern Illinois to Minnesota, and along the eastern Appalachian Mountains. Lower concentrations were also observed in coastal North Carolina and Florida. The western sites measured low concentrations – most with values less than 0.5 μg/m^3.

Figure 2-20 presents a box plot of NH_4^+ concentrations aggregated from the eastern United States 34-site reference database. The data show a slight reduction in annual NH_4^+ values over the 11-year period.

Changes in 3-year average NH_4^+ concentrations are presented in Figure 2-21. All but six of the CASTNet reference sites measured decreases in NH_4^+ levels. The largest decreases were observed in the Midwest.

Peak NH_4^+ concentrations were observed in the Midwest, Pennsylvania, and northern Alabama. The data show a slight reduction in annual mean NH_4^+ values over the last 11 years.

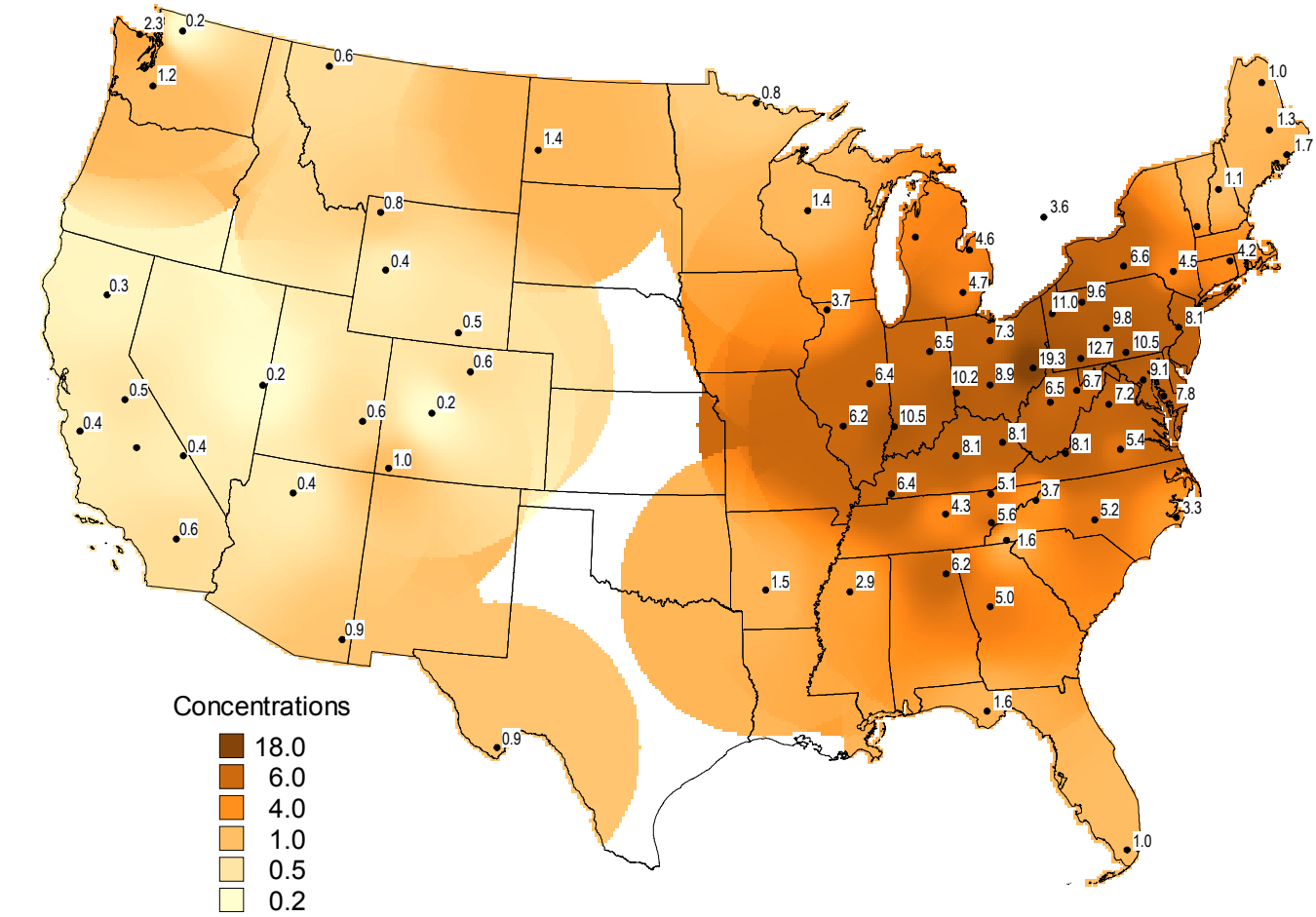
Cations

Annual mean concentrations of Ca^{2+}, K^+, Mg^{2+}, and Na^+ for 2000 are shown in Figures 2-22 through 2-25. Two geographic patterns are evident from the four maps. First, the highest Ca^{2+} concentrations were measured in the agricultural Midwest, extending into Ontario. Other areas with high Ca^{2+} concentrations extend along the Atlantic coast from North Carolina to the Everglades, FL. Relatively high concentrations were also measured in Speedwell, TN (SPD111), Big Bend National Park, TX (BBE401), and at JOT403. Figure 2-25 shows that the highest Na^+ concentrations were measured on or near the coastal plain. Concentrations above 0.25 μg/m^3 were observed from the Everglades to Acadia National Park (ACA416) in Maine. The monitor at Pinnacles National Park, CA (PIN414) measured an annual mean of 0.54 μg/m^3, and the site at Olympic National Park, WA (OLY421) measured a concentration of 0.38 μg/m^3.

An analysis of cation measurements suggests two geographic patterns. First, the highest Ca^{2+} concentrations were measured in the agricultural Midwest. Second, the highest Na^+ concentrations were observed on or near the coastal plain from Florida to Maine and in California and Washington. No patterns were observed for potassium and magnesium.

Note: In the following figures, the concentration shading was prepared using an algorithm based on inverse distance cubed weighting with a radius of influence of 500 km. Consequently, concentration estimates for areas near the geographic limits of site coverage have no meaning (e.g., western Missouri). Shading was not prepared for Alaska, Hawaii, and the Virgin Islands.

Figure 2-1. Annual Mean SO_2 Concentrations ($\mu g/m^3$) for 2000



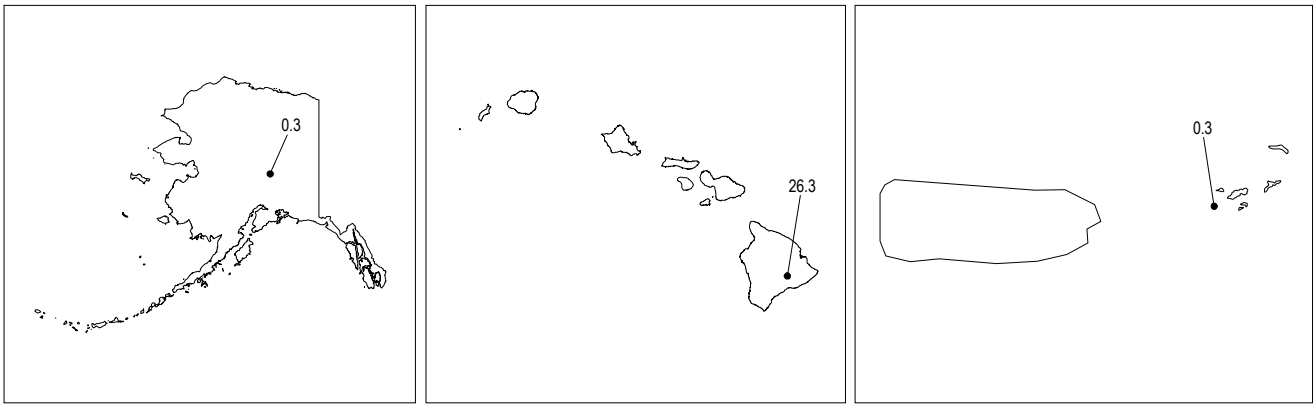


Figure 2-2. Trend in Annual SO_2 Concentrations – Eastern United States

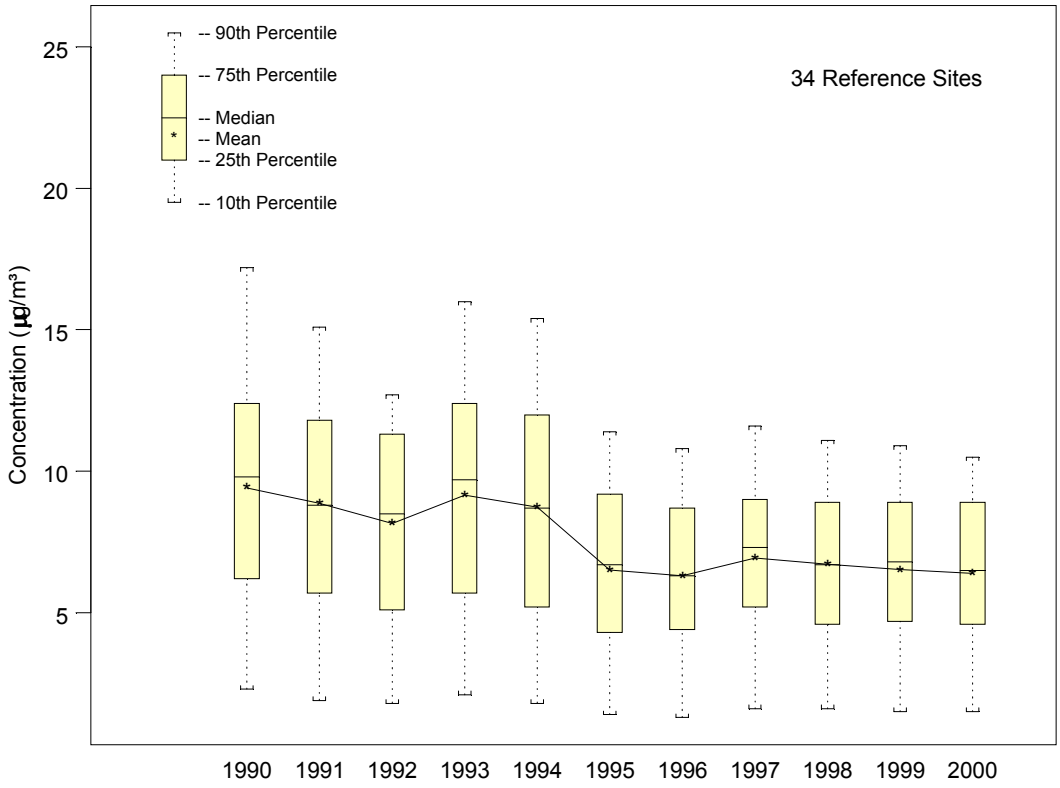


Figure 2-3. Differences in 3-Year Mean SO_2 Concentrations (1990-1992 versus 1998-2000)

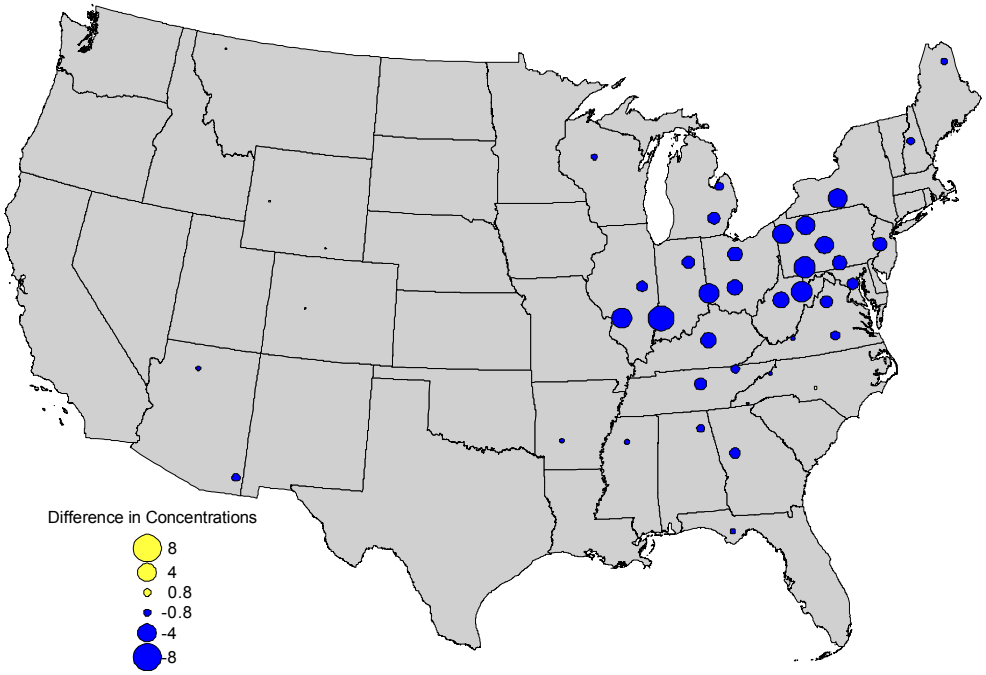


Figure 2-4. Annual Mean Particulate SO_4^{2-} Concentrations (µg/m^3) for 2000

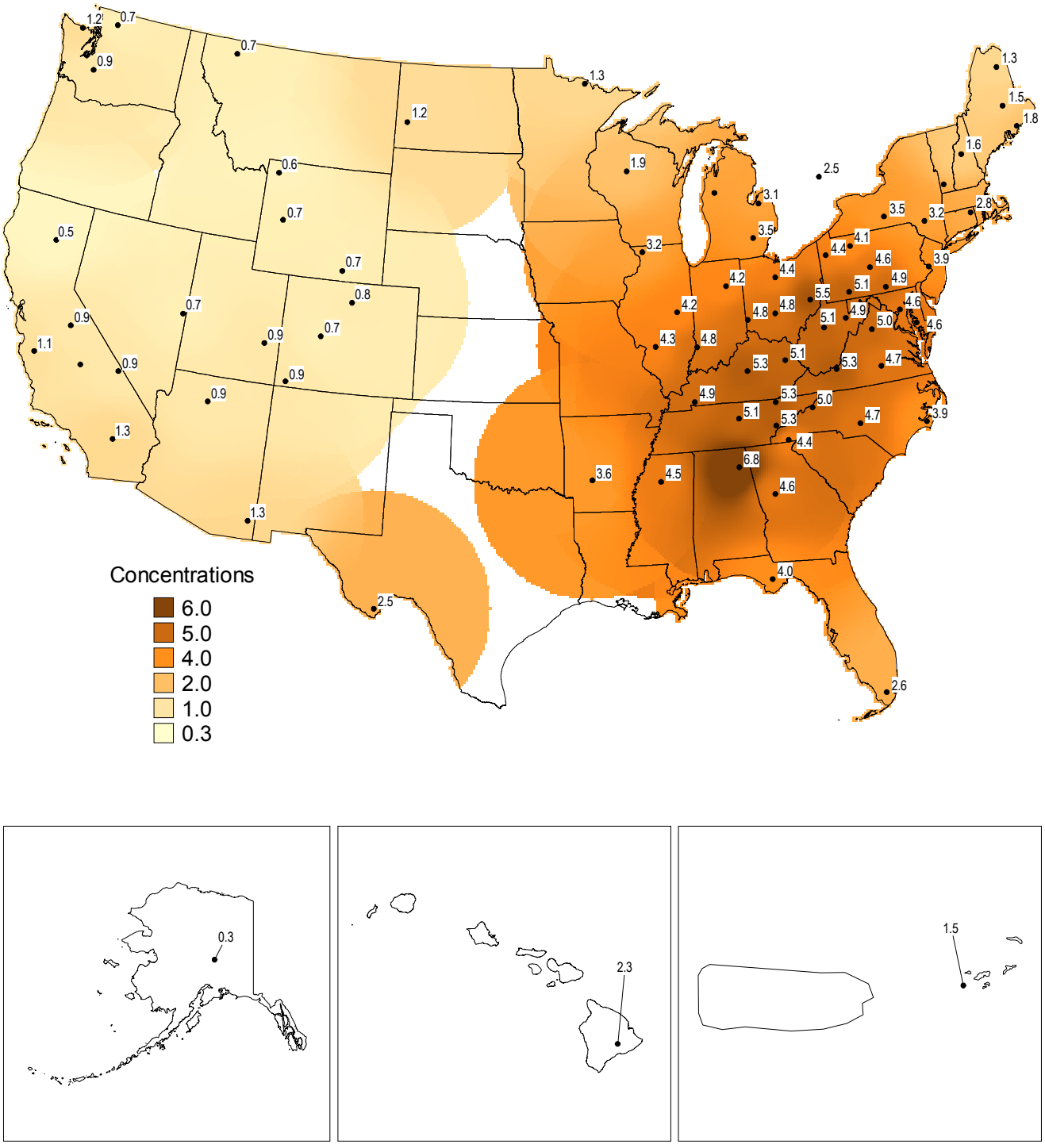


Figure 2-5. Annual Mean Particulate SO_4^{2-} Concentrations ($\mu g/m^3$) for 1991

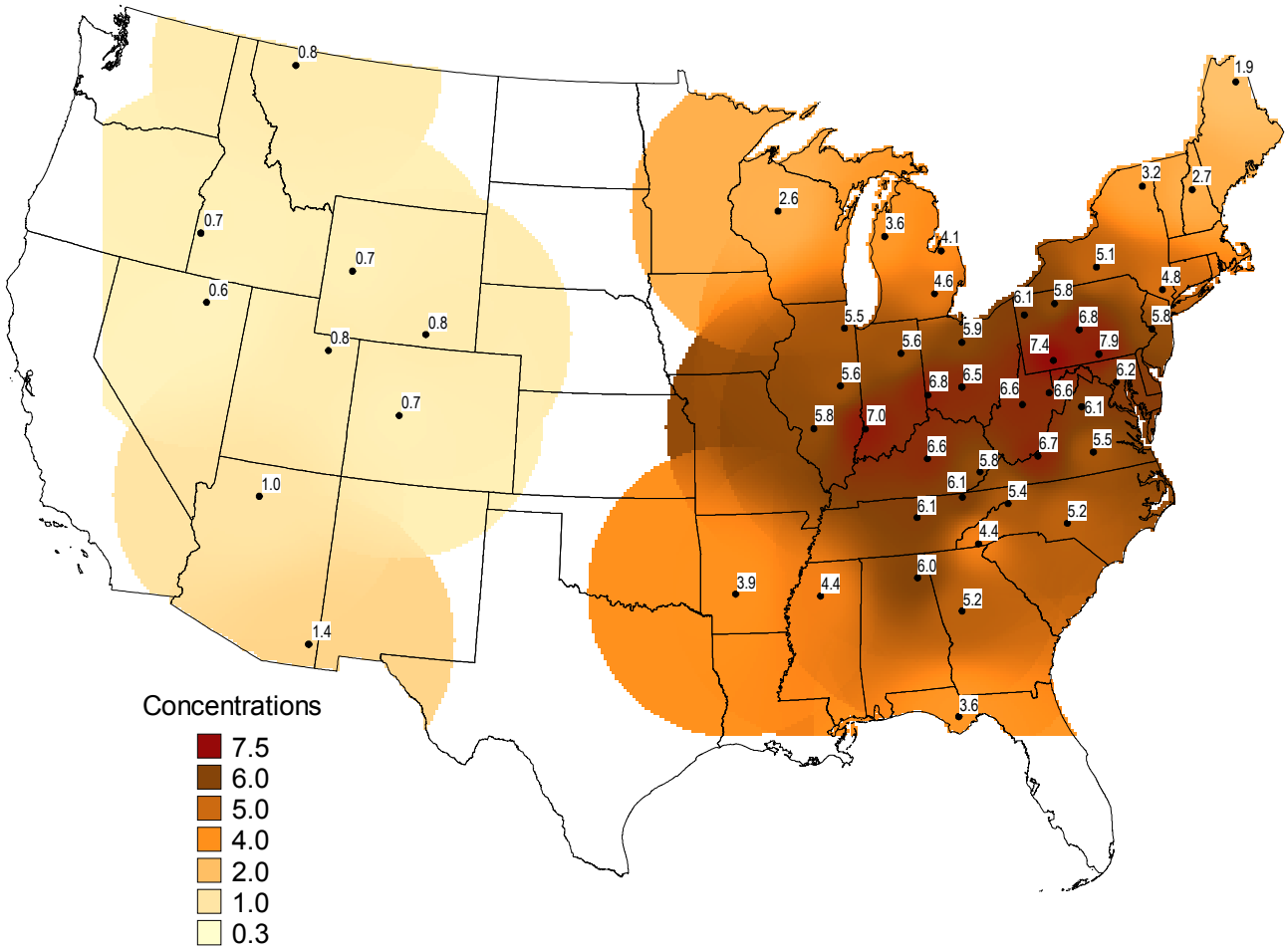


Figure 2-6. Trend in Annual SO_4^{2-} Concentrations – Eastern United States

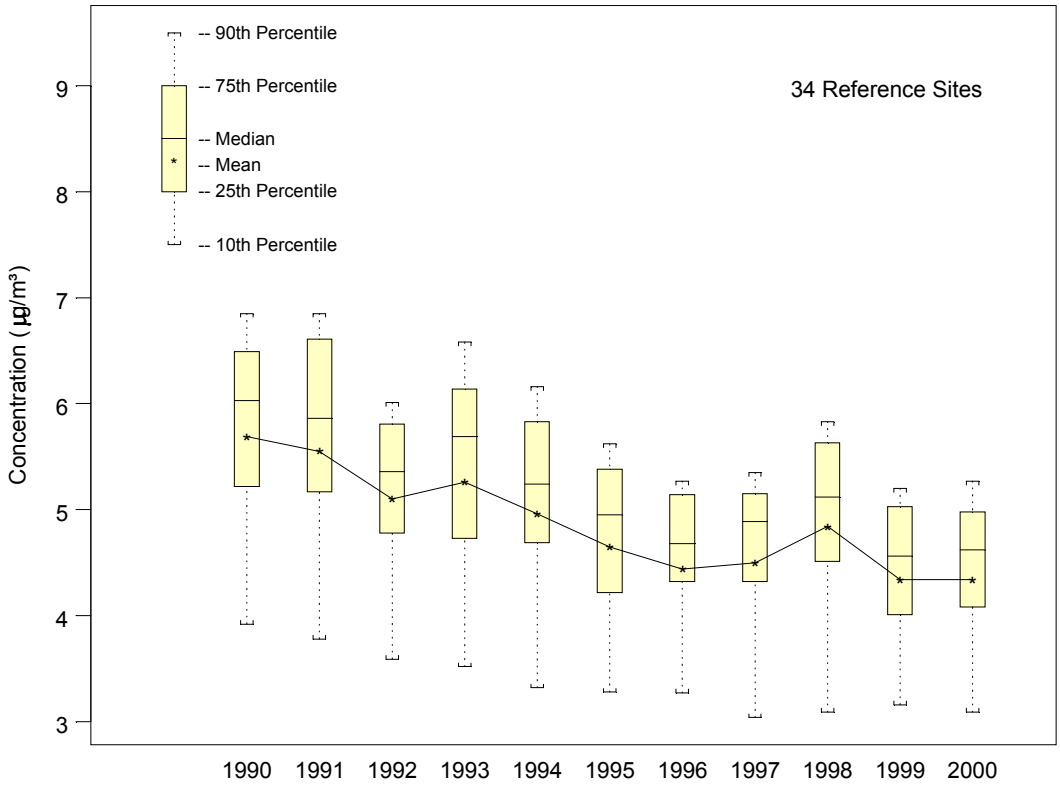


Figure 2-7. Differences in 3-Year Mean SO_4^{2-} Concentrations (1990-1992 versus 1998-2000)

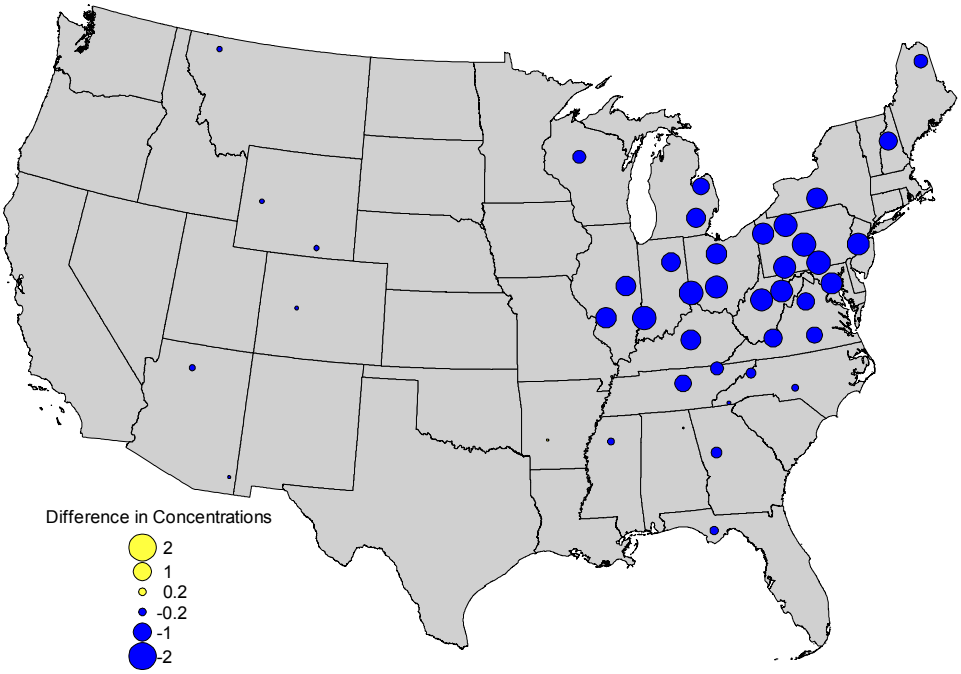
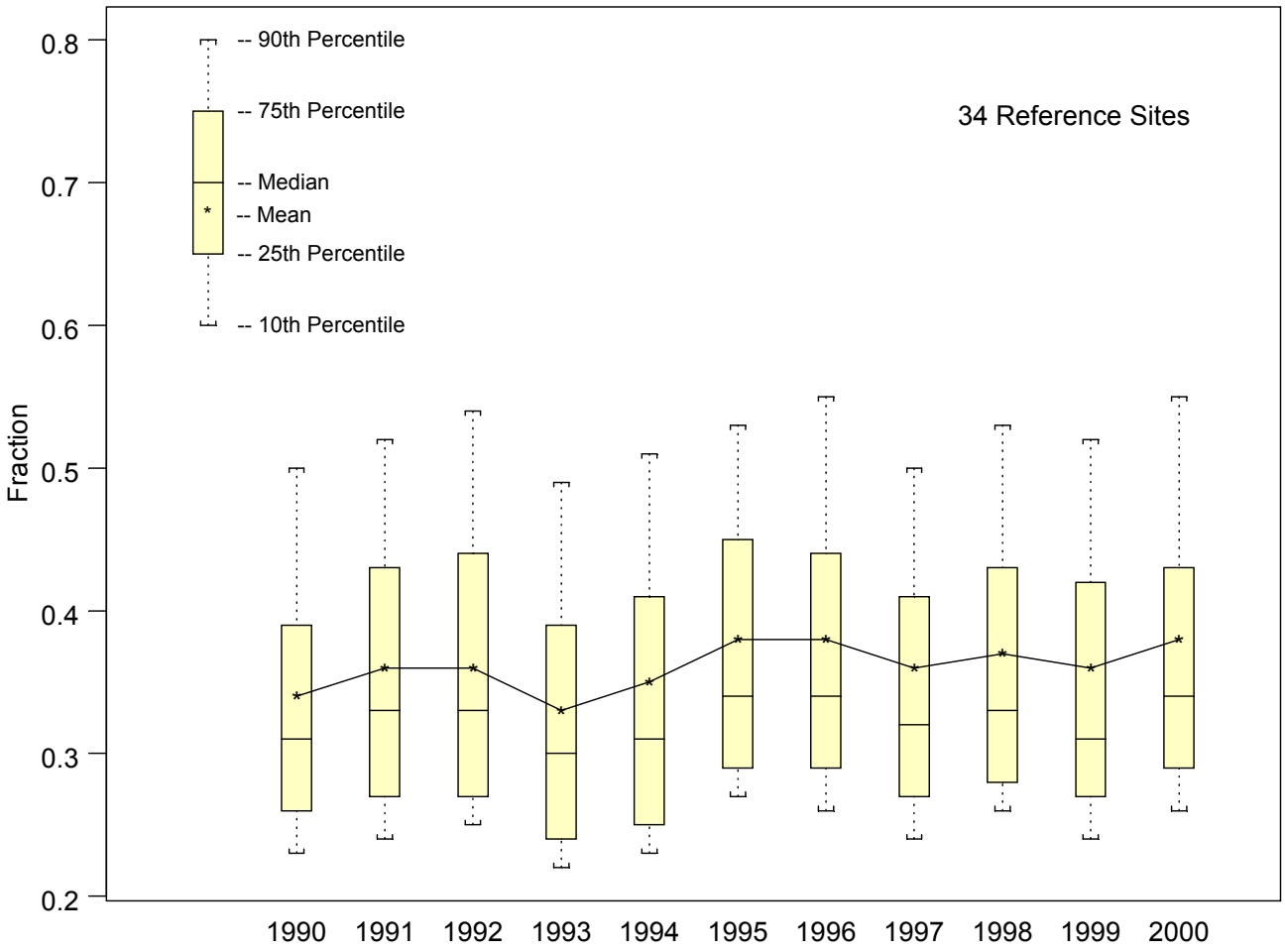


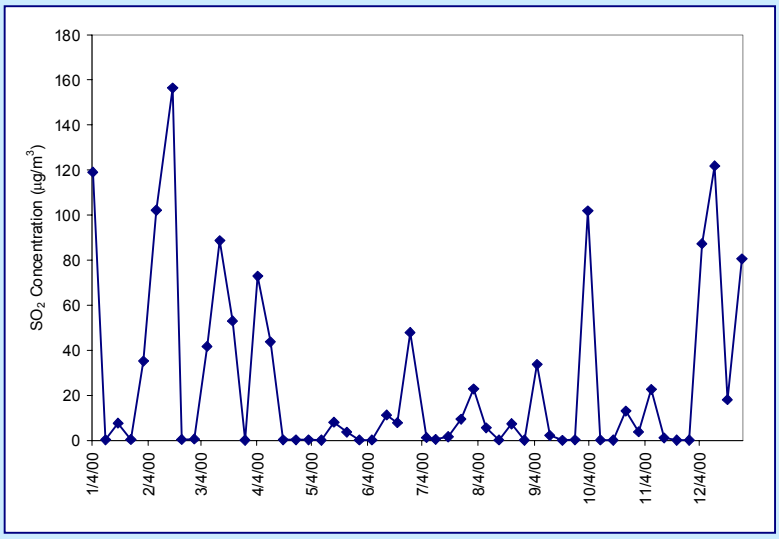
Figure 2-8. Fraction of SO_4^{2-} as S in Total Sulfur (SO_4^{2-} + SO_2, as S) – Annual Values – Eastern United States



Sulfate concentrations have decreased more slowly than SO_2 concentrations, though both are produced by SO_2 emissions. Reid et al. (2001) suggest an incomplete understanding of atmospheric sulfur compounds and the link between SO_2 emissions and aerosol SO_4^{2-}.

Kilauea Volcano: A Source of SO_2

Kilauea, located on the Big Island of Hawaii, is one of the world's most active volcanoes. The volcano is situated within Hawaii Volcanoes National Park. The park is also home to CASTNet site HVT424, which provides air quality data that show the atmospheric affects of an active volcano. Kilauea, which has been in a stage of continuous eruption since 1983, is a major natural source of SO_2 pollution in Hawaii.



Deep beneath the ground, a volcano's magma contains gases dissolved at extremely high pressure. As the magma travels closer to the surface, the pressure decreases, allowing the gases to form bubbles within the magma. In some cases the gas bubble volume may exceed the melt volume of the magma, creating magma foam. The rapidly expanding gas in this foam can lead to explosive activity, thereby releasing the trapped gases. If no explosive activity occurs, a lava flow will develop. In this case, the trapped gases may still be released when the magma cools and breaks apart upon entering the sea. It is a common occurrence for the volcanic gases of Kilauea to be released through ocean entry and explosive activity. Given that 11.8 percent of volcanic gas is SO_2, there is great potential for air pollution from the steady lava flow [see the U.S. Geological Survey (USGS) site for more information on volcanic gases]. http://volcanoes.usgs.gov/Hazards/What/VolGas/volgas.html

Results from CASTNet site HVT424 show eight episodes of heightened SO_2 concentrations on the Big Island during 2000. Comparing the dates of high lava flow (gathered from http://hvo.wr.usgs.gov/kilauea/update/archive/main.html, a USGS site that archives Kilauea activity) with periods of high SO_2 concentrations shows a strong correlation between increased lava flow and high levels of atmospheric SO_2. The 2000 total mean SO_2 concentration for CASTNet sites in the continental United States is 4.3 $\mu g/m^3$, with the highest value of 19.3 $\mu g/m^3$ measured in eastern Ohio. Hawaii's recorded SO_2 concentrations range from 0.14 $\mu g/m^3$ to 156.41 $\mu g/m^3$, with a mean concentration of 26.44 $\mu g/m^3$. As demonstrated by the time series of weekly SO_2 levels (above), Hawaii's CASTNet site showed periods of extremely low SO_2 concentrations followed by periods of extremely high SO_2 concentrations. The first episode of high SO_2 concentrations in early January marked the third highest weekly SO_2 concentration for the site for 2000. This surge in concentrations followed a prolonged period of steady lava flow into the ocean during December 1999. The second episode, spanning a few weeks of February 2000, showed the highest SO_2 concentration for the entire year. This peak coincided with additional ocean entries of the lava flow, leading to increased release of SO_2. The third and fifth episodes correspond to periods of high fume levels above Kilauea's crater. The rest of the episodes all occur during periods of increased lava flow and ocean entry, demonstrating that the release of volcanic gas produces high levels of SO_2 concentrations near the volcano.

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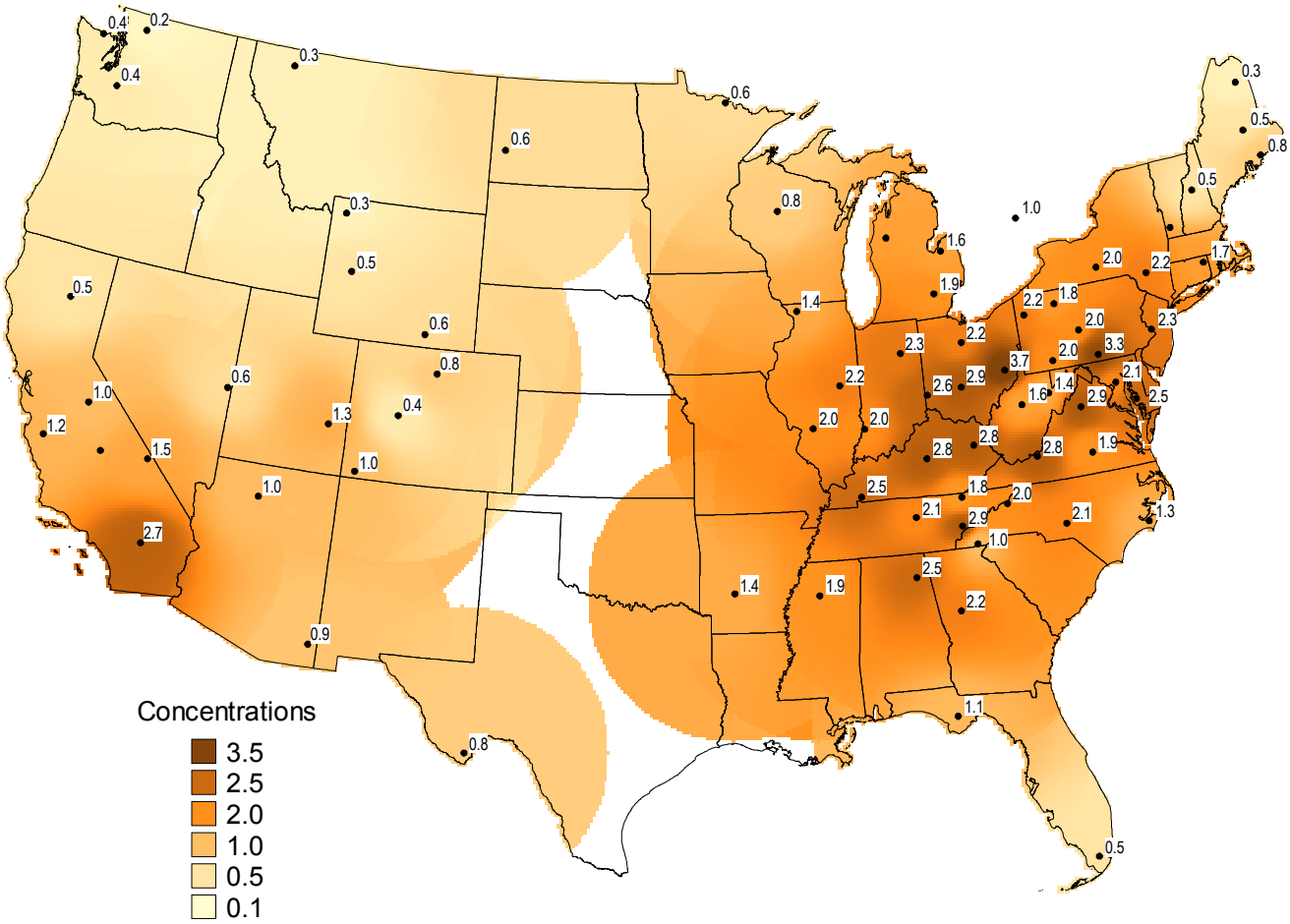
Figure 2-9. Annual Mean HNO_3 Concentrations ($\mu g/m^3$) for 2000



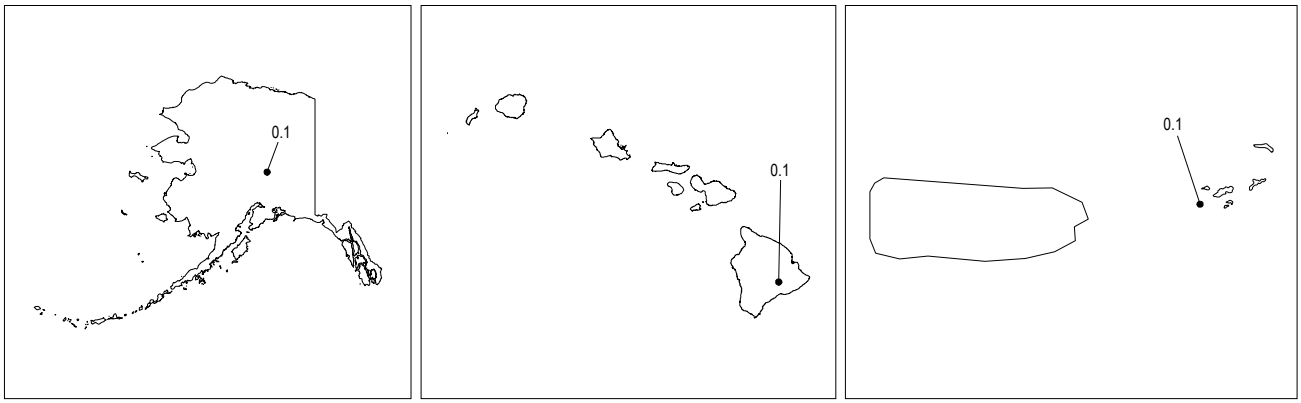


Figure 2-10. Trend in Annual HNO_3 Concentrations – Eastern United States

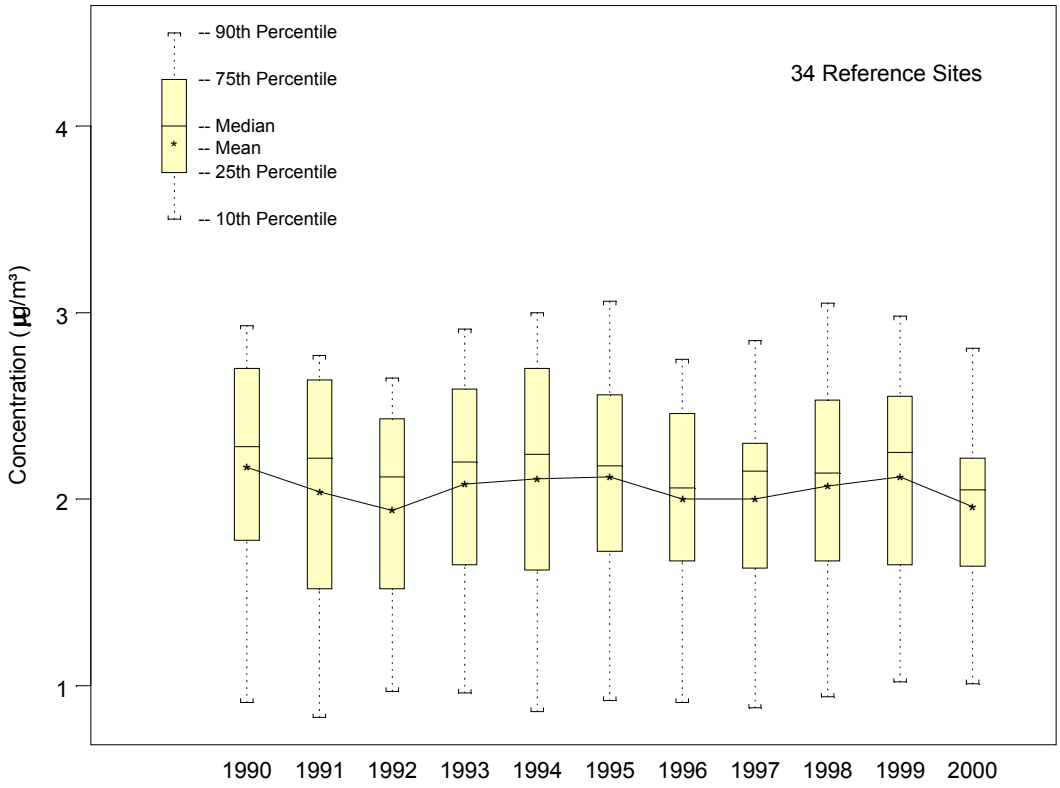


Figure 2-11. Differences in 3-Year Mean HNO_3 Concentrations (1990-1992 versus 1998-2000)

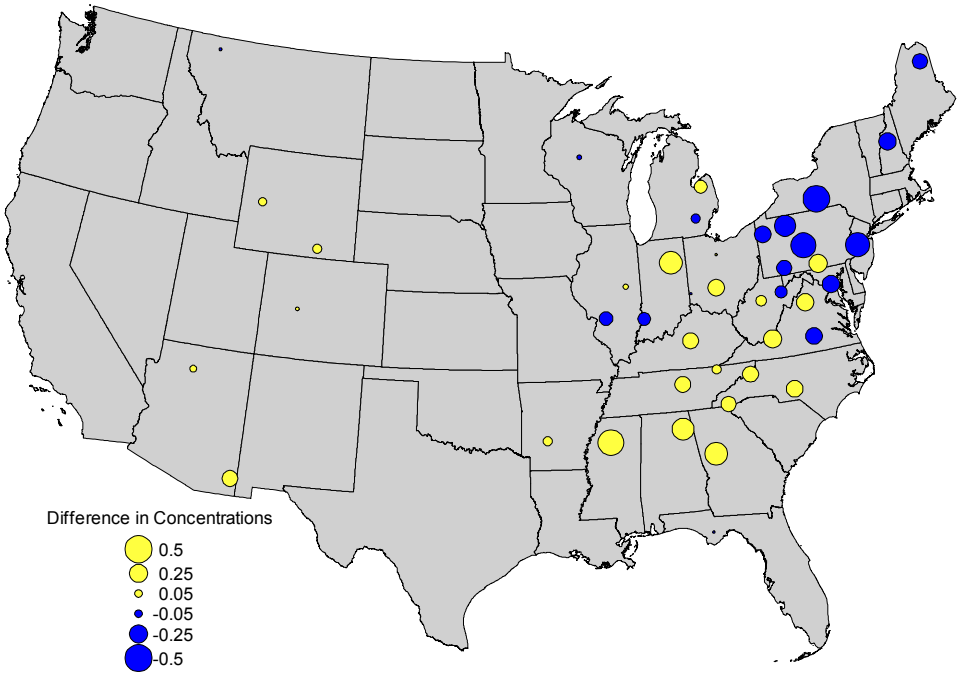
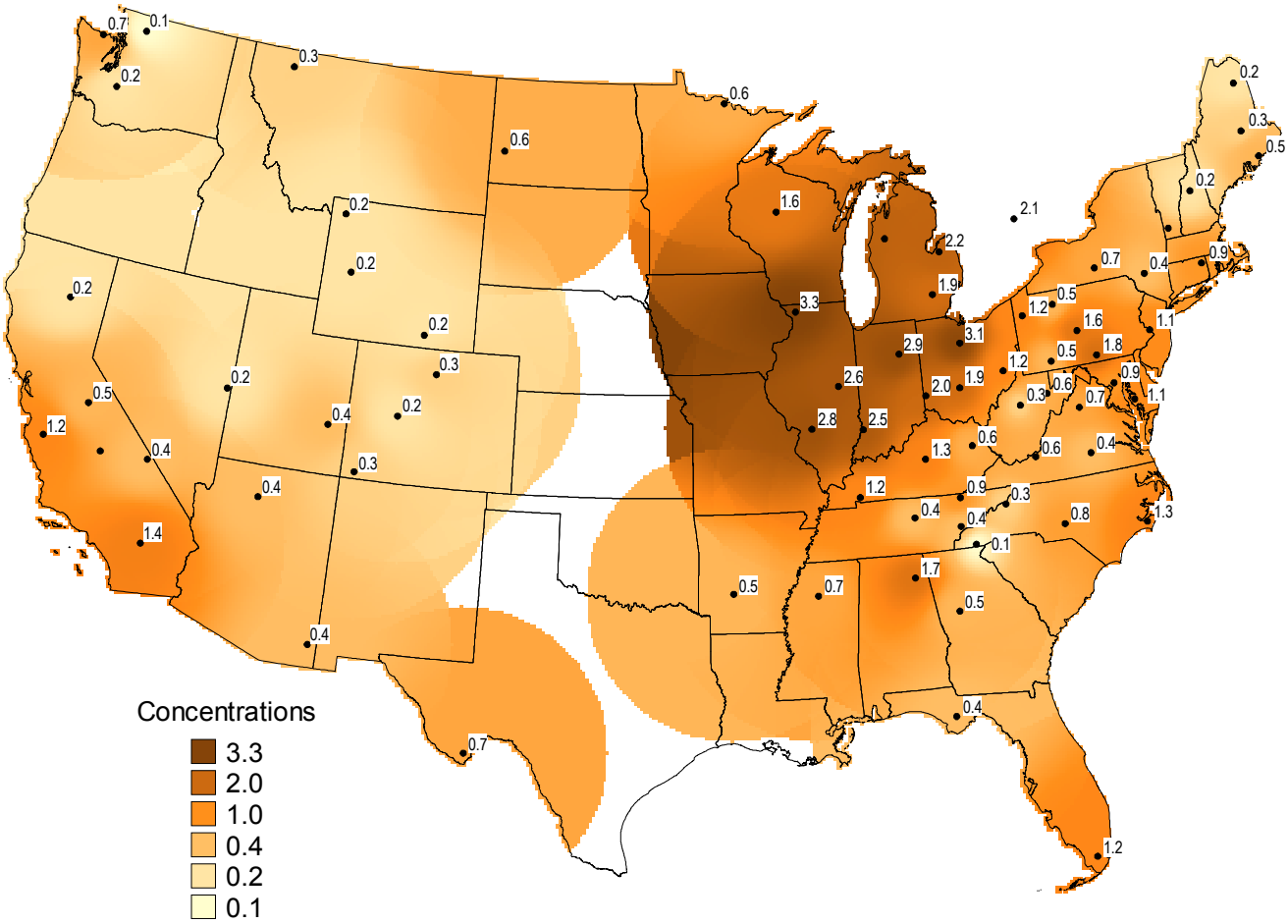


Figure 2-12. Annual Mean Particulate NO_3^- Concentrations ($\mu g/m^3$) for 2000



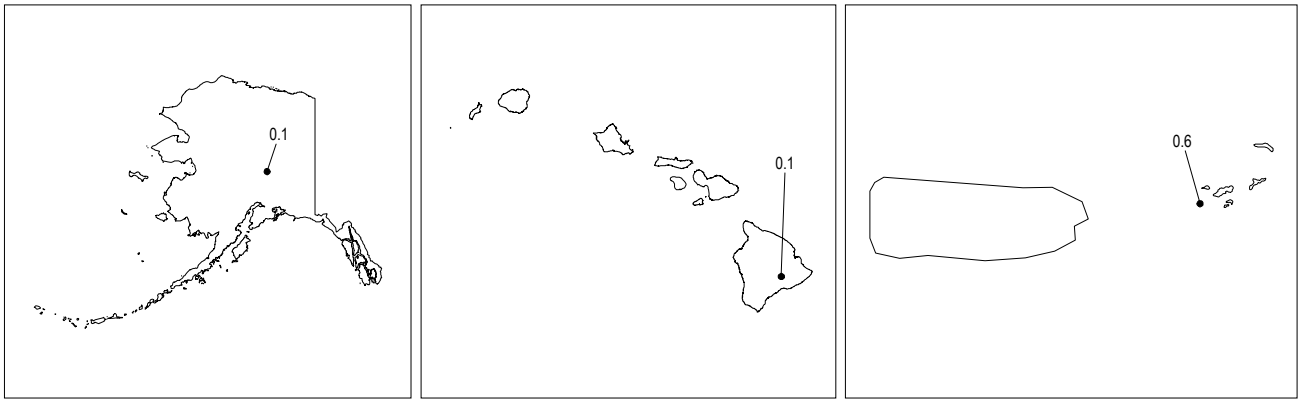


Figure 2-13. Trend in Annual NO_3^- Concentrations – Eastern United States

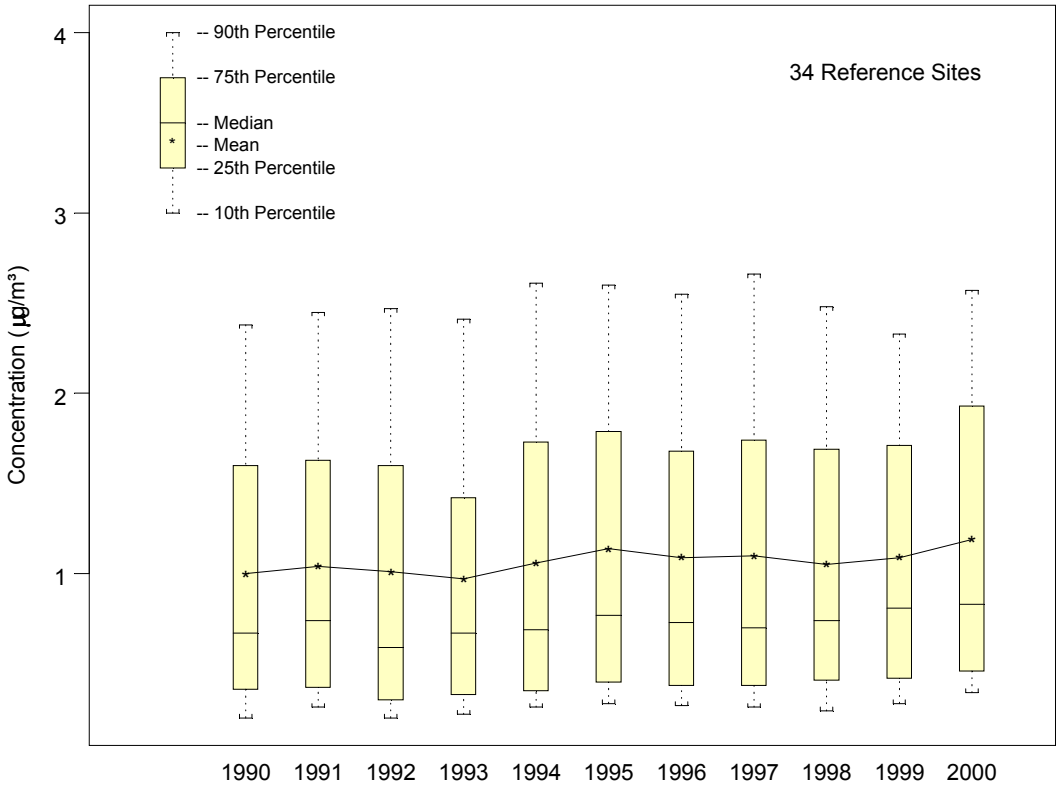


Figure 2-14. Differences in 3-Year Mean NO_3^- Concentrations (1990-1992 versus 1998-2000)

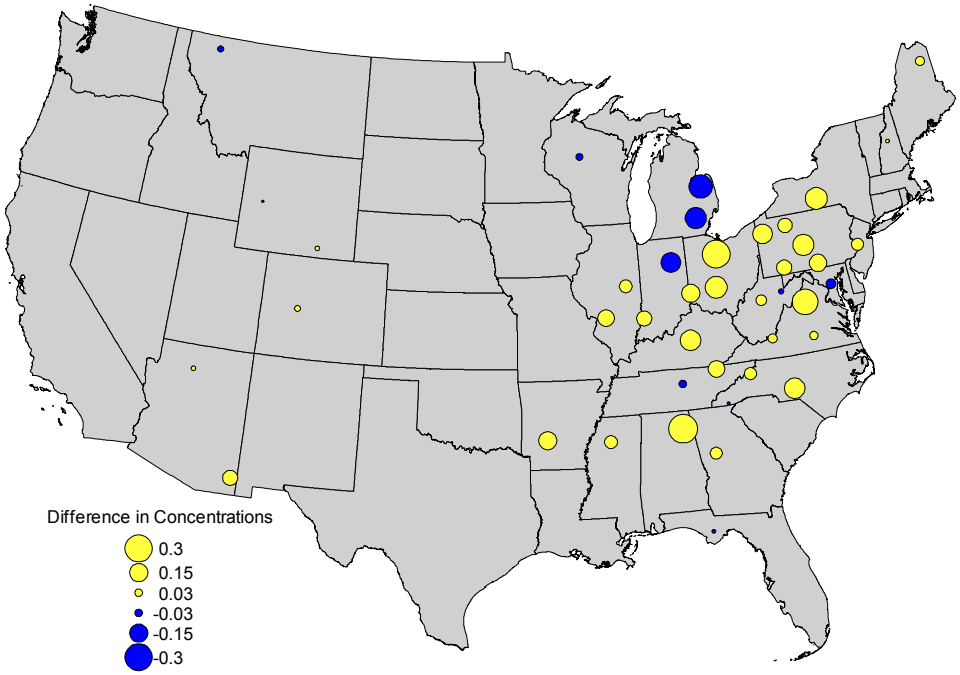


Figure 2-15. Annual Mean Total NO_3^- Concentrations ($\mu g/m^3$) for 2000

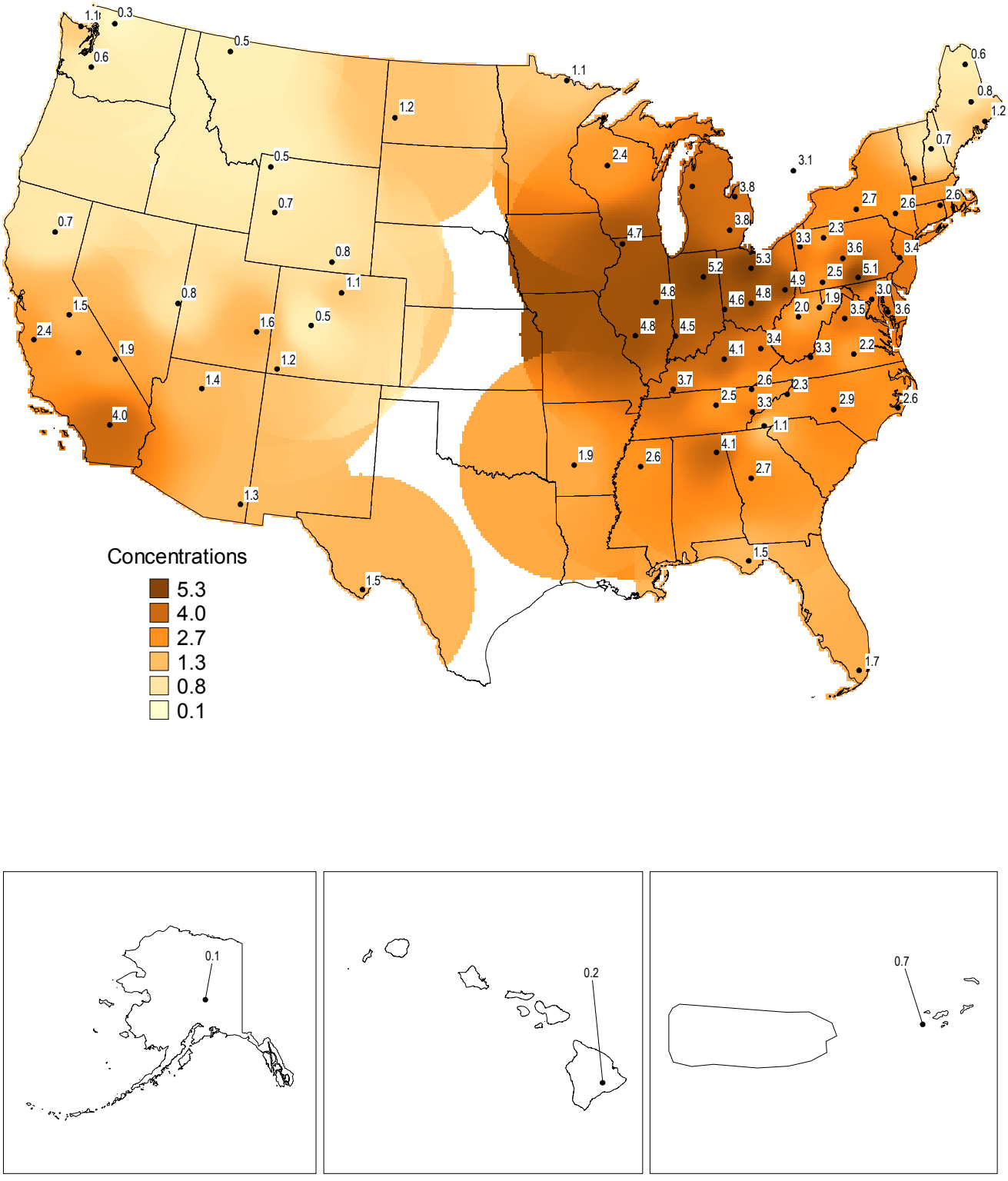


Figure 2-16. Trend in Annual Total NO_3^- Concentrations – Eastern United States

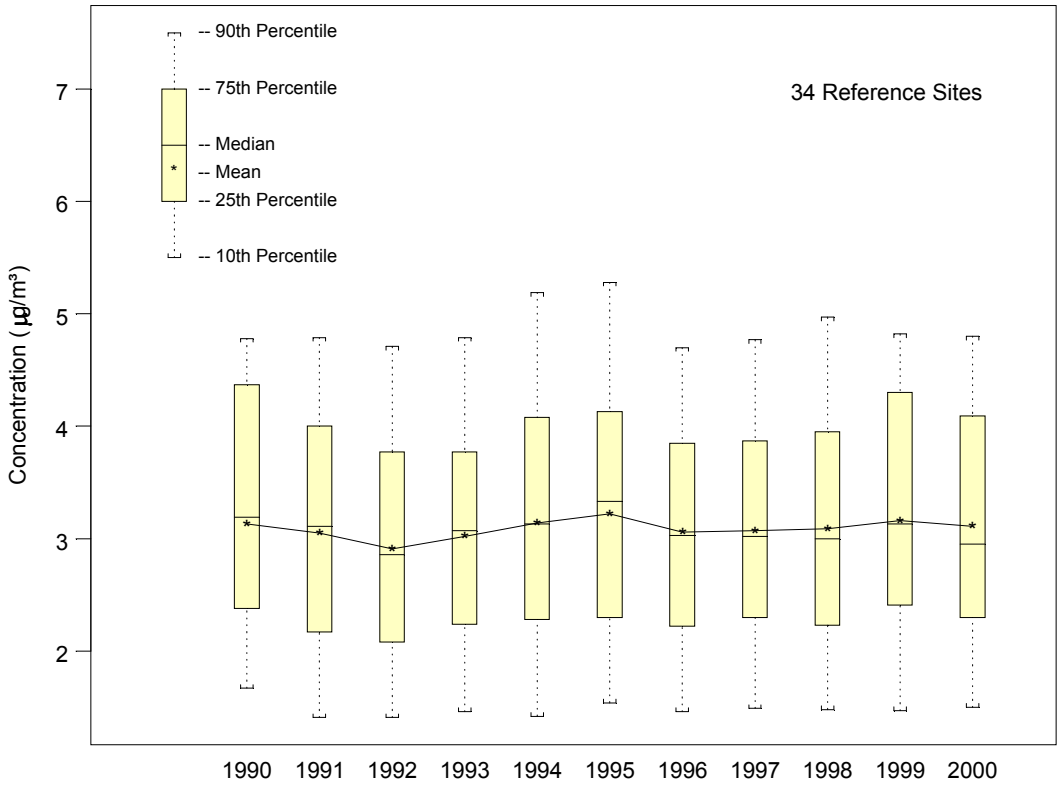


Figure 2-17. Differences in 3-Year Mean Total NO_3^- Concentrations (1990-1992 versus 1998-2000)

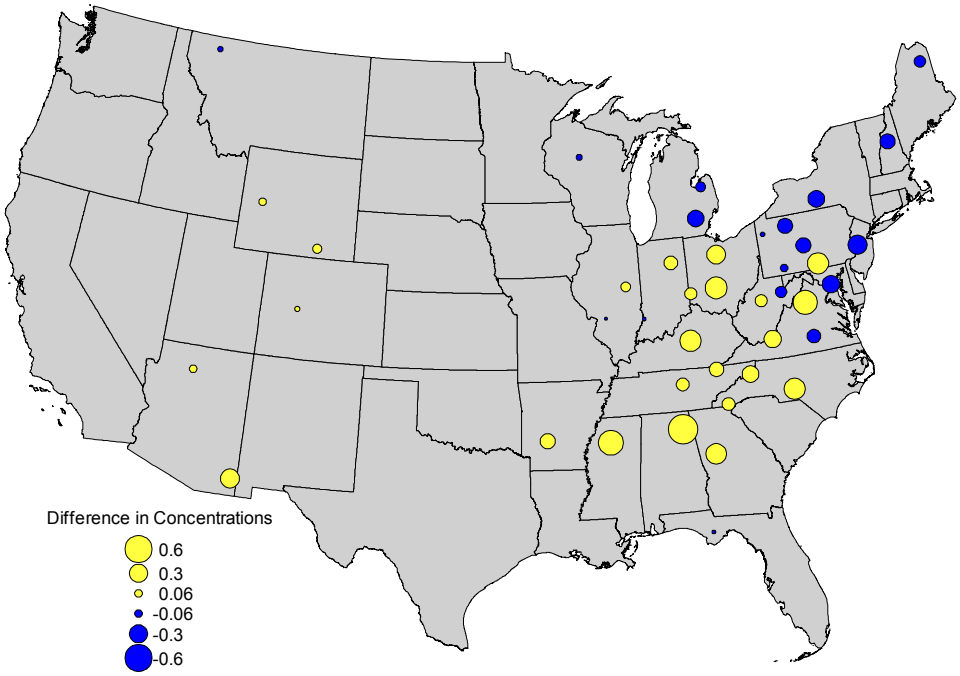
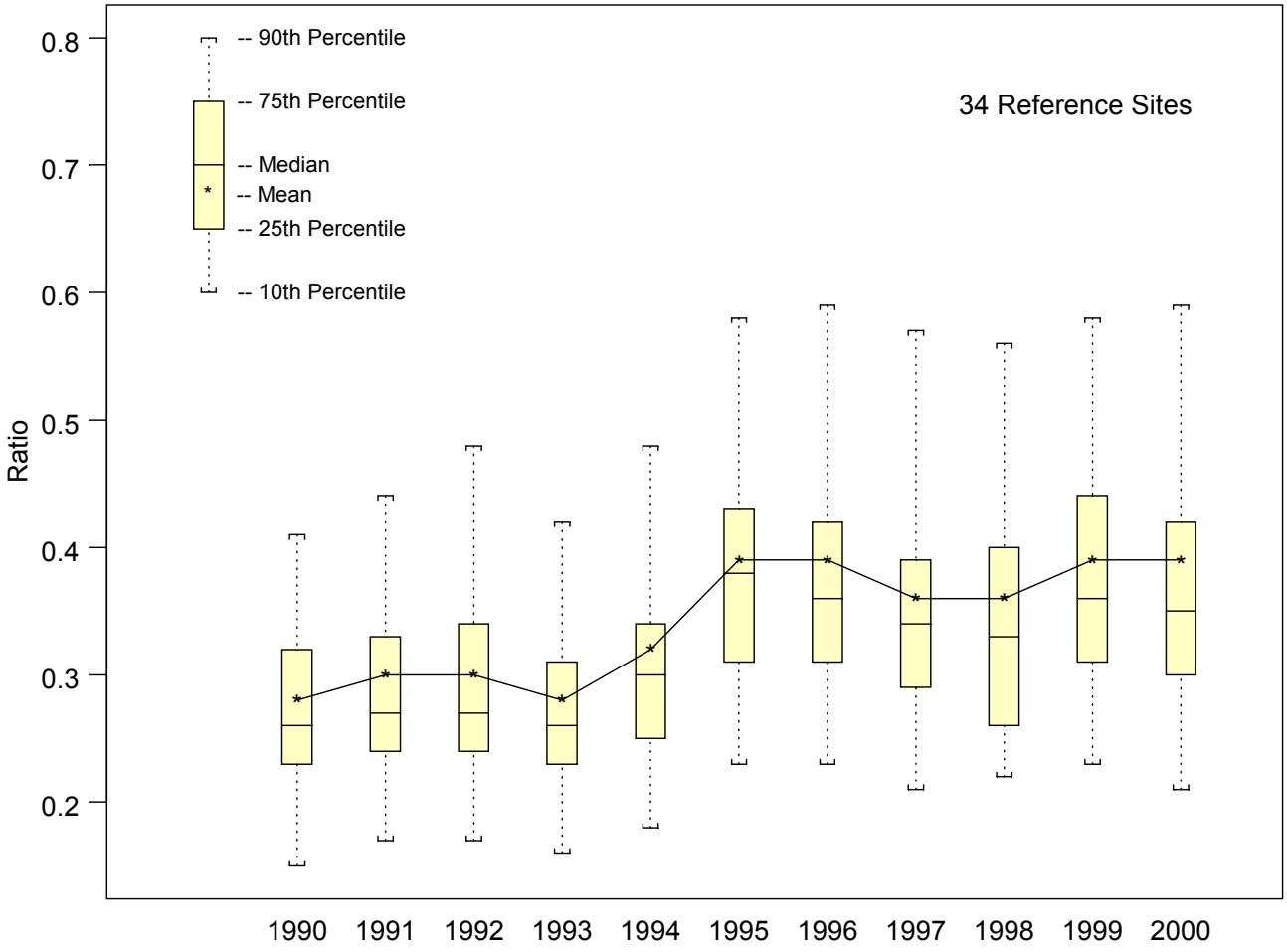


Figure 2-18. Ratio of Nitrogen to Sulfur Concentrations (molar weights) – Eastern United States



Nitrogen-sulfur ratios show an increase in the nitrogen fraction following changes in NO_x and SO_2 emissions.

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Figure 2-19. Annual Mean Particulate NH_4^+ Concentrations ($\mu g/m^3$) for 2000

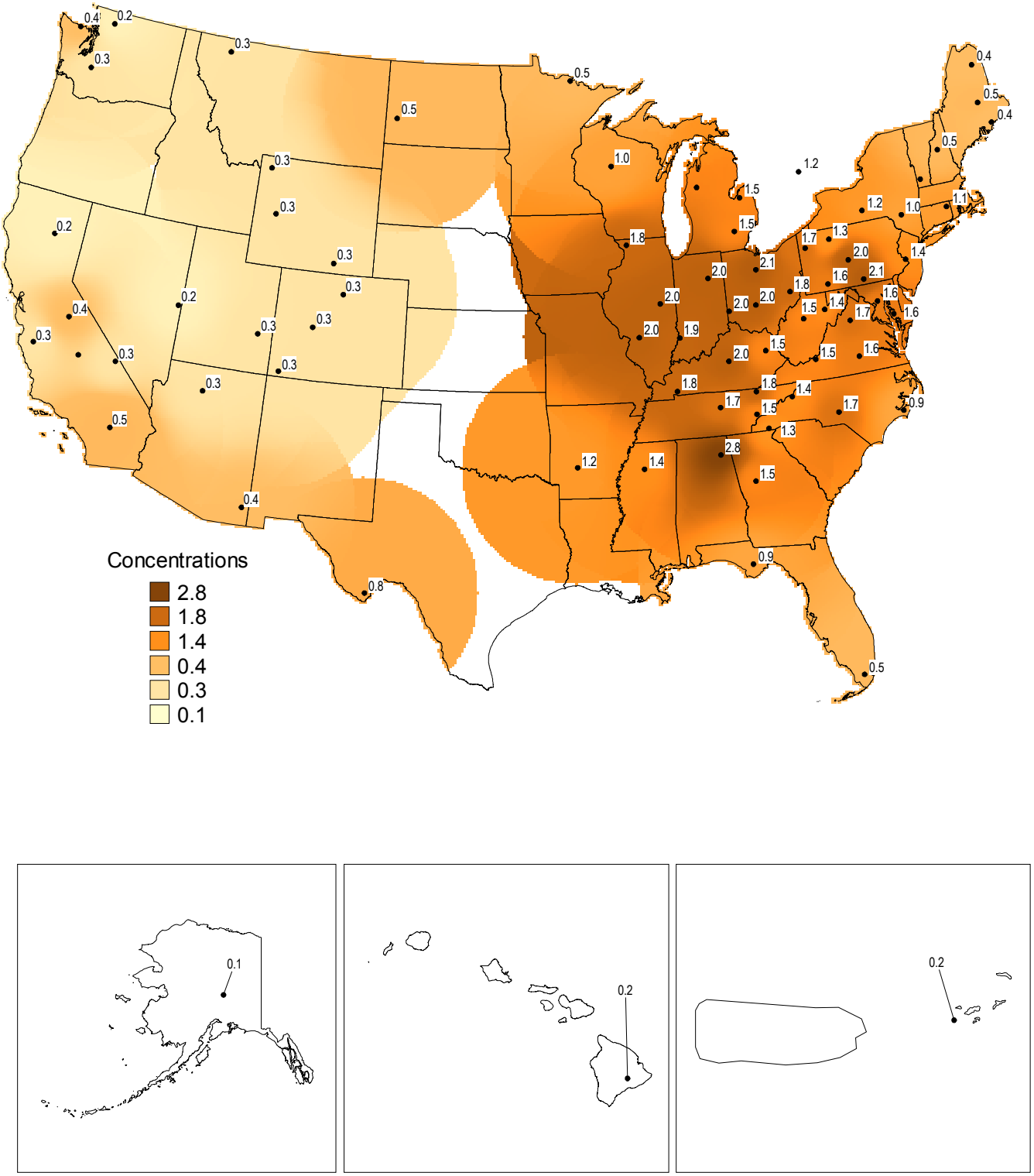


Figure 2-20. Trend in Annual NH_4^+ Concentrations – Eastern United States

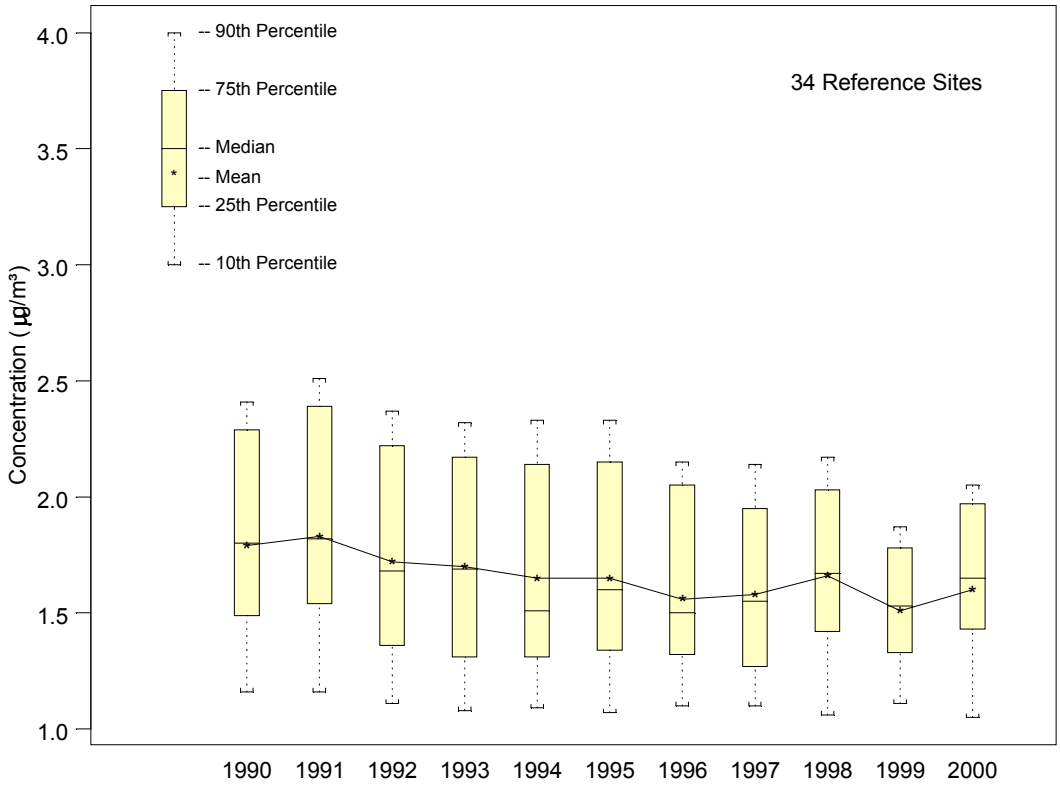


Figure 2-21. Differences in 3-Year Mean NH_4^+ Concentrations (1990-1992 versus 1998-2000)

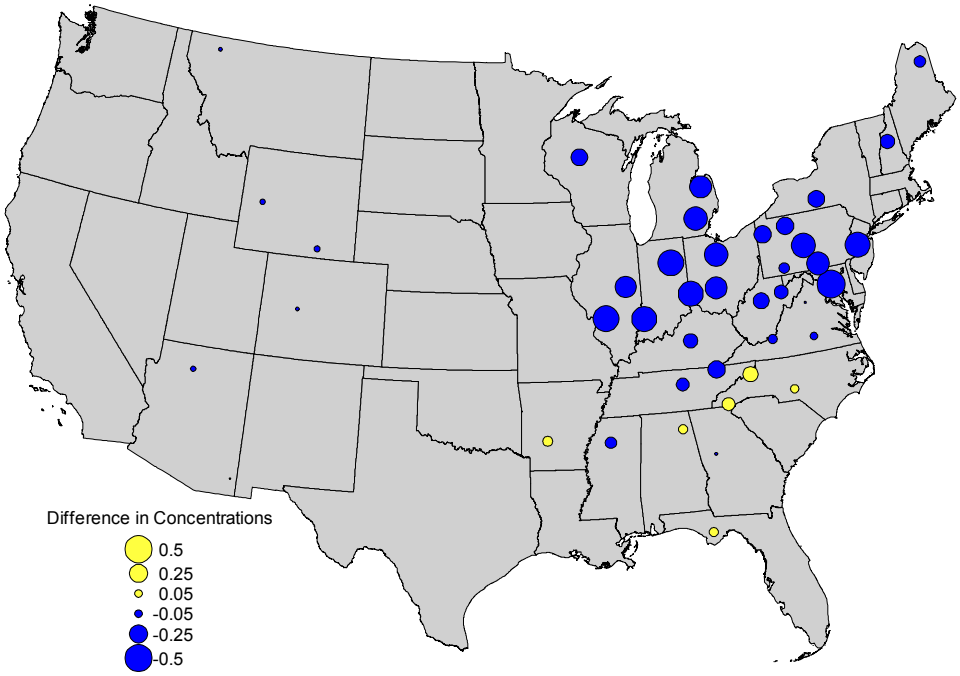
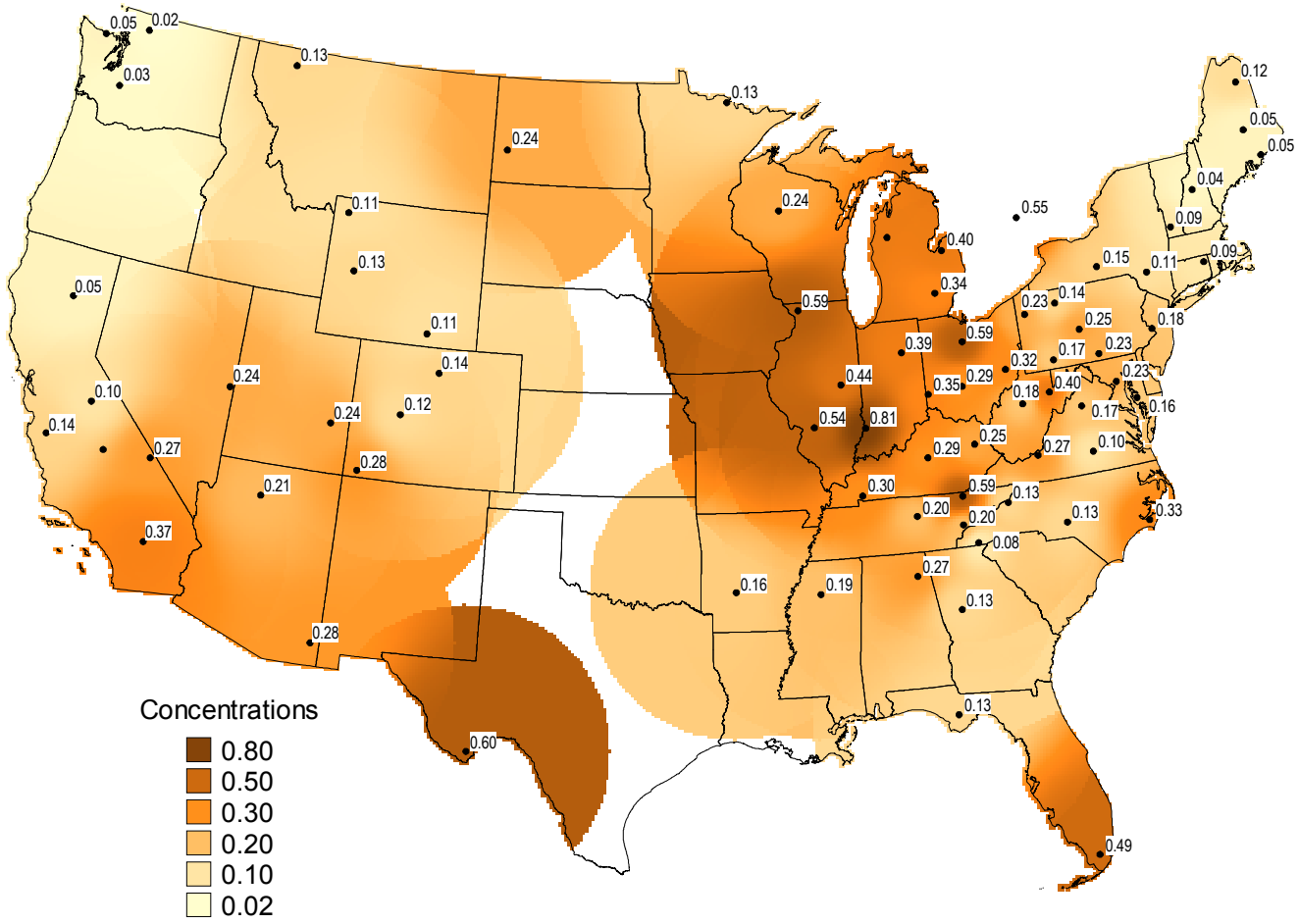


Figure 2-22. Annual Mean Particulate Ca^{2+} Concentrations ($\mu g/m^3$) for 2000



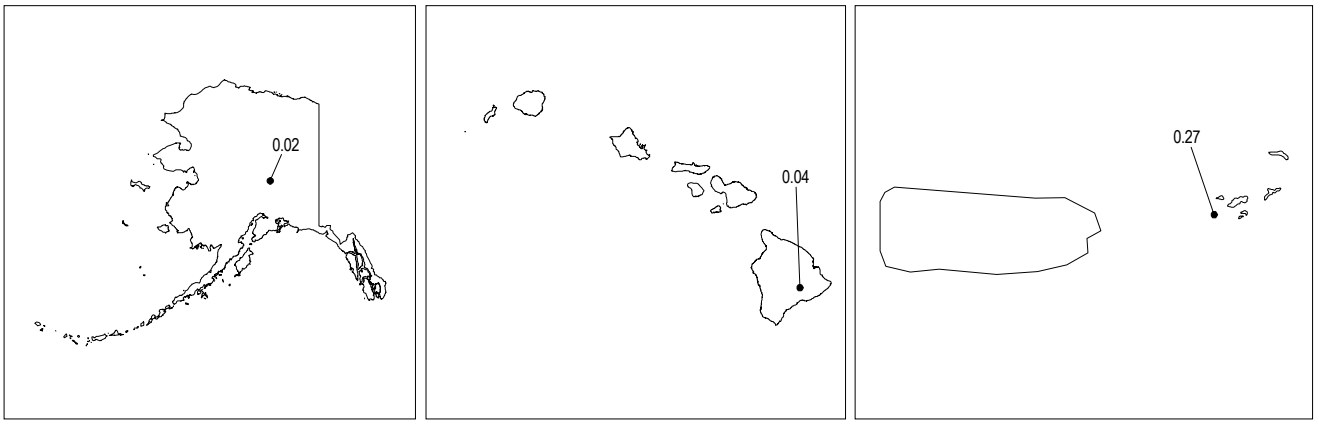


Figure 2-23. Annual Mean Particulate K^+ Concentrations ($\mu g/m^3$) for 2000

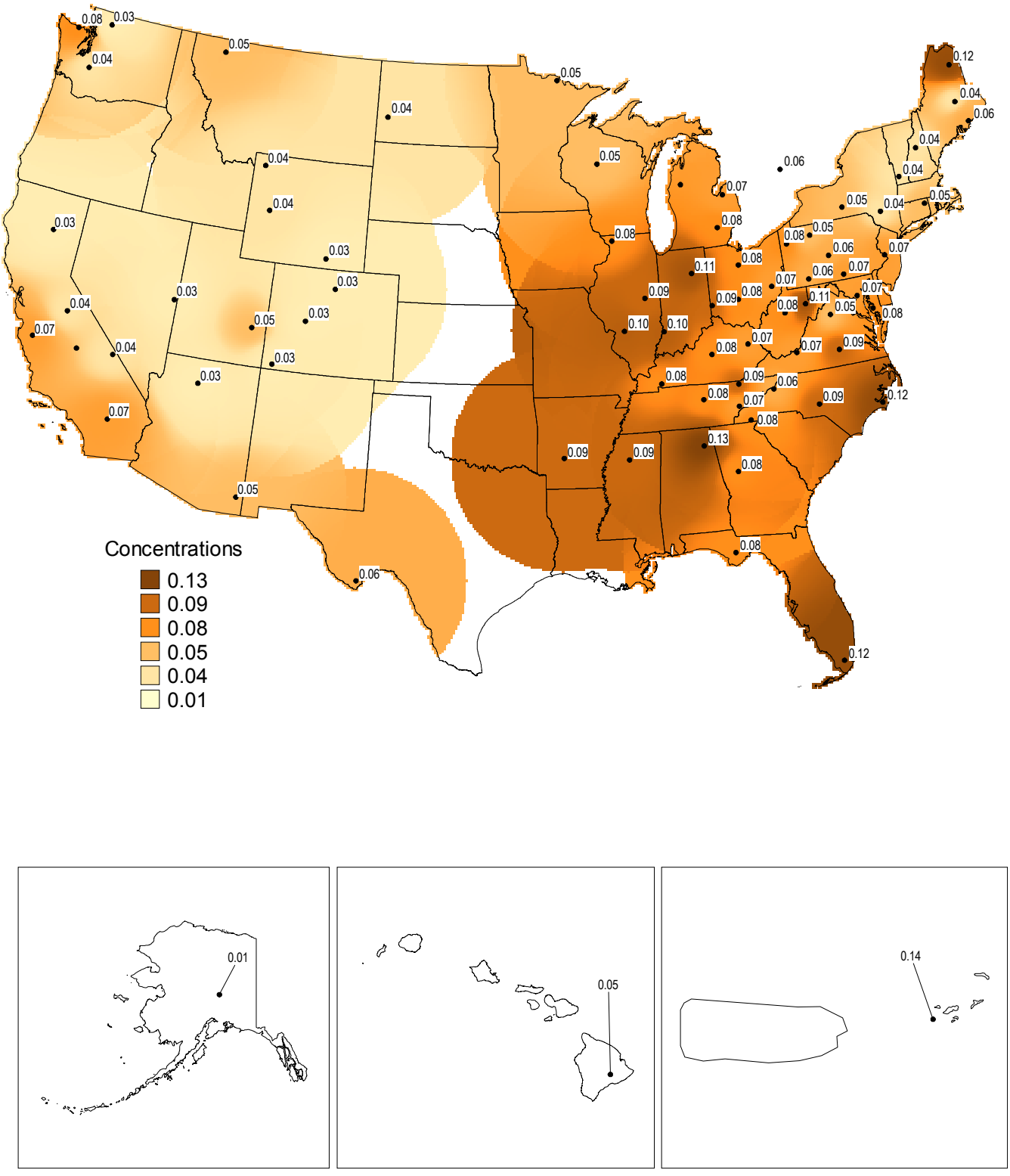


Figure 2-24. Annual Mean Particulate Mg^{2+} Concentrations ($\mu g/m^3$) for 2000

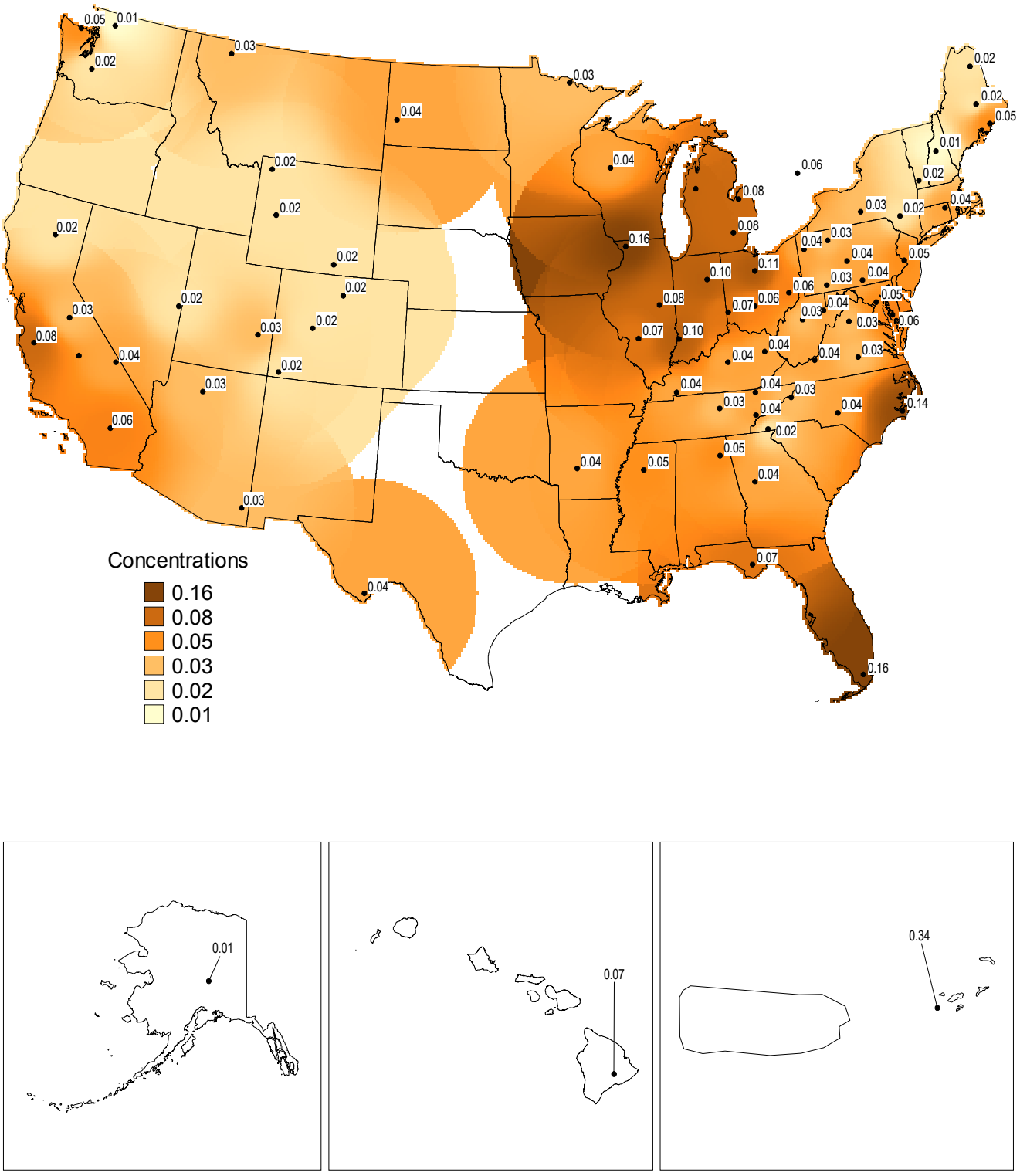


Figure 2-25. Annual Mean Particulate Na^+ Concentrations ($\mu g/m^3$) for 2000